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MEASUREMENTS OF THE SIZE DISTRIBUTION AND SOLUBILITY OF SALTY D-ETC(U)
AUG 81 W A HOPPEL, T A WOJCIECHOWSKI
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MEASUREMENTS OF THE SIZE DISTRIBUTION AND SOLUBILITY OF SALTY DOG PYROTECHNIC

BACKGROUND

Several pyrotechnic formulations which upon burning produce hygroscopic aerosols have been developed by the Naval Weapons Center. The advantage of a hygroscopic aerosol is that particles swell by the addition of water vapor at relative humidities above 70% to produce larger particles and a more effective obscurant in most naval environments than is possible for nonhygroscopic aerosols of the same total dry mass. For more background information on advantages and characteristics of hygroscopic aerosols see the referenced reports. One of the more successful pyrotechnic formulations and the one considered in this report is a formulation developed by NWC called Salty Dog.

A laboratory investigation of the particle size distribution produced by combustion of Salty Dog and the deliquescent growth of individual large particles was undertaken by Hanley and Mack (1980) at Calspan Corporation. Two results of the Calspan study are important to the background of this investigation: (1) Calspan found that only about a third of the Salty Dog consumed by combustion could be accounted for in the aerosol measurements and

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(2) the size distributions measured at various relative humidities seemed to indicate that only the larger particles in the size distribution ($r > 0.15 \mu\text{m}$) were growing with increasing relative humidity. The smaller particles ($r < 0.15 \mu\text{m}$) seemed to show little to no change in size with relative humidity.

Subsequent to Calspan's report two hypotheses were advanced to explain these results. (1) The process of combustion usually produces large numbers of very small particles. Some of the missing mass was postulated to be in the very small size range and not adequately accounted for in the measurements. (2) Recondensation of Salty Dog material into aerosol particles after burning produces an aerosol in which the smaller sizes have much less soluble material (or a surface-active coating), while larger particles contain more of the soluble material. Hanley and Mack (1980) had looked only at the solubility of giant size particles ($10 \mu\text{m}$ radius) which are much larger than the average size produced by combustion of Salty Dog.

NRL has developed under their atmospheric aerosol and cloud physics program unique instrumentation to look at very small atmospheric aerosol particles (Hoppel 1978). It was decided to utilize this instrumentation for a laboratory investigation to test these two hypotheses.

OBJECTIVE

The relationship between the saturation ratio S (relative humidity divided by 100) and the equilibrium radius r for a partly

soluble nucleus of dry size r_d is given by Fitzgerald (1975).

$$S = \text{Exp} \left(\frac{2 \sigma'}{r \rho' RT} \right) \left[1 + \frac{1 \epsilon \rho_d M_w r_d^3}{M_s \rho' \{r^3 - r_d^3 (1-\epsilon) - \epsilon \frac{\rho_s}{\rho'} r_d^3\}} \right]^{-1}$$

where σ' and ρ' are the surface tension and density of the droplet, ρ_d is the density of the dry particle, M_w and M_s are the molecular weights of water and the soluble salt, and ϵ is the fraction of soluble material which has a solubility given by the van't Hoff factor i .

At high values of the saturation ratio the solution is dilute and the two terms of Eq. (1) can be expanded to yield the familiar expression.

$$S = 1 + \frac{A}{r} - \frac{B_o r_d^3}{r^3} \quad (2)$$

where $A = \frac{2\sigma'}{\rho' RT} \quad (3)$

and $B_o = \frac{1\epsilon \rho_d M_w}{M_s \rho_w} \quad (4)$

where ρ_w is the density of water. At a certain supersaturation ($RH > 100\%$) a particle is nucleated and grows continuously to cloud droplet sizes. The value of supersaturation necessary to nucleate the particle is called the critical supersaturation and depends upon the size and solubility of the particle. The critical supersaturation S_c obtained by differentiating Eq. (2) is

$$S_c = \left(\frac{4}{27} - \frac{A^3}{B_o r_d^3} \right)^{1/2} \quad (5)$$

This expression relates the dry size r_d of a nucleus to the critical supersaturation necessary for activation and is important in transforming aerosol dry size distributions to CCN supersaturation spectra and vice versa. For pure salt particles of NaCl and $(NH_4)_2SO_4$, this expression has recently been found to agree well with values obtained experimentally (Gerber, et al. 1977).

NRL has developed a mobility analyzer for the accurate measurement of the aerosol size distribution down to $0.005 \mu m$ radius (Hoppel, 1978). In addition this instrument can be used as an aerosol classifier to separate out and transmit particles in a very narrow size range. When the mobility analyzer is used in this mode particles of a known

dry size can then be transmitted to the NRL thermal gradient diffusion cloud chamber (TGDC) where the critical supersaturation S_c necessary to nucleate them can be measured. This procedure provides us with both S_c and r_d so that the solubility parameter B_o can be calculated from Eq. (5). This method has been used to obtain important information on the solubility of ambient atmospheric aerosols at various geographical locations.

Equation (1) which gives the relationship between relative humidity and equilibrium size can be written in terms of B_o in the following form:

$$S = \text{Exp} \left(\frac{A}{r} \right) \cdot \left[1 + \frac{B_o r_d^3}{\frac{\rho'}{\rho_w} r^3 - r_d^3 (1-\epsilon) - \epsilon \frac{\rho_d}{\rho} r_d^3} \right]^{-1} \quad (6)$$

It is clear from Eq. (6) that in addition to B_o , ϵ and ρ_d must also be known to obtain S as a function of r . However if ρ' is also expressed in terms of ϵ , ρ_w , and ρ_d and if the sensitivity of Eq. (6) to various values of ϵ and ρ_d is studied numerically, it is found that Eq. (6) is very insensitive to ϵ and ρ_d over ranges of these variables expected in hygroscopic aerosols. This means that using an

experimental value of B_0 in Eq. (6) together with any reasonable value of ϵ and ρ_d will give the relative humidity dependence of the equilibrium size. This relationship will hold only for relative humidities above the deliquescent point of the salty dog aerosol ($\sim 80\%$).

The objective of this study was then twofold. To produce a Salty Dog aerosol and (1) measure the size distribution accurately at small sizes to see if significant amount of mass was contained in small sizes. (2) to measure the solubility of the small aerosols by the B_0 method described. This measurement would test the hypotheses that the smallest aerosols are less soluble than the larger particles measured by Calspan.

EXPERIMENTAL PROCEDURE AND RESULTS

Figure 1, shows a diagram of the experimental set-up. Salty Dog was ignited in a bell jar by an electric heating element while the jar was being ventilated with ultrapure compressed air from a cylinder. The amount of material burned was varied from 80 to 200 milligrams.

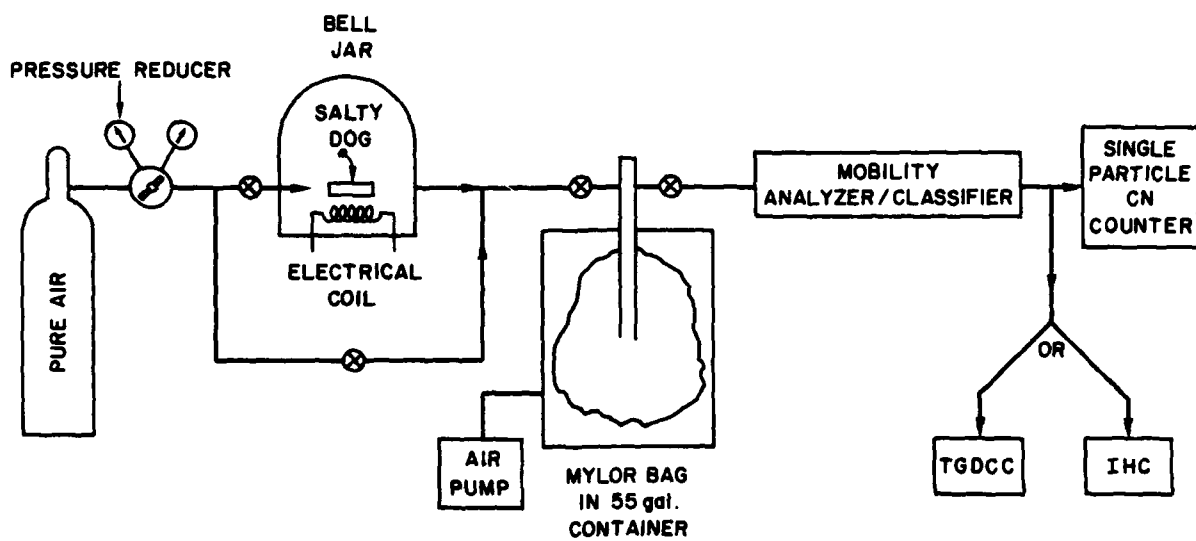


Fig. 1 — Schematic of experimental arrangement

The aerosol was passed into a metallized mylar bag with an inflated capacity of about 100 liters. The size distribution from about 0.005 μm to 1 μm radius was measured with the mobility analyzer and from about 0.27 to 3 μm with a Royco Optical particle counter. The measurement of the size distribution took about 15 minutes after which aerosols of a known size were transmitted to the TGDCC to determine what supersaturation (S_c) was required for nucleation. From this result B_0 was to have been calculated from Eq. (5).

Early results indicated there was a negligible number of particles less than about 0.2 μm in radius produced in our system. This did not agree with the size distribution presented by Calspan who ignited their pyrotechnique with a propane torch in a much larger chamber. Variations of our experiment were tried in an attempt to generate significant numbers of smaller particles. The amount of salty dog burned was varied from about 80 mg to 200 mg. Burning more created particle concentrations so large that dilution to measureable concentrations was difficult; whereas burning less than about 100 mg made the burn so short (< 1 sec) that it is doubtful it could be representative of larger burns. In most burns we used about 100 to 120 mg. Since the aerosol particles are formed by recondensation of material into particles it was thought that blowing the incoming air directly over the burning Salty Dog might immediately dilute the vaporized material and produce smaller particles by recondensation.

This was tried and still the number of particles smaller than about $0.2\text{ }\mu\text{m}$ was negligible. If smaller particles were formed initially in the vicinity of the burning material, these particles grew by coagulation or further condensation and formed larger particles within the 5 minutes required to fill and dilute the aerosol in the bag. We were unable to reproduce the size distribution given by Calspan in our laboratory scale experiment. Possible reasons for this difference are many including such differences as: (1) Scale. Calspan's chamber is very large (600 m^3) and the aerosol may have been diluted more rapidly and growth by coagulation stifled. (2) Ignition process. Calspan used a propane torch to ignite the Salty Dog whereas we used an electrical heating element. We measured the aerosol size distribution produced by our glowing, red-hot wire in pure air and found it to contain only very small particles. All particles were smaller than about $0.02\text{ }\mu\text{m}$ with most particles about $0.007\text{ }\mu\text{m}$ in radius. Interestingly, all evidence of these small particles disappeared when Salty Dog was burned. This of course is expected since these small aerosols have very high diffusion coefficients and would have attached to the Salty Dog aerosols very rapidly. (3) Size of burn. The duration, uniformity and temperature of the burn can be expected to influence the size distribution. Despite the possible reasons for the difference in the size distributions measured by Calspan and NRL, our inability to produce small particles ($< 0.2\text{ }\mu\text{m}$ radius) under a variety of conditions warrants further investigation in the future as to the physical origin of the difference.

The typical cumulative size distribution obtained in our experiments is shown by the solid line in Figure 2. We believe the instrumental errors are small for particles with radii below $1.0\text{ }\mu\text{m}$. However, considering the size of our plumbing and storage bag and the time required to carry out our experiment, we estimate considerable loss of particles by sedimentation for sizes greater than $2\text{ }\mu\text{m}$. Therefore, the number of particles larger than $2\text{ }\mu\text{m}$ is certainly understated in our experiment. This probably leads to a significant steeping of the size distribution at larger sizes.

Because we found no particles smaller than $0.2\text{ }\mu\text{m}$ it was not possible to carry out the measurement of the solubility parameter B_0 for the small particles as proposed. Therefore, we thought it would be instructive to measure the solubility of particles with sizes in the range where most particles were generated in our experiment ($0.2\text{ }\mu\text{m}$ to $0.5\text{ }\mu\text{m}$). This size particle is still well below the $10\text{ }\mu\text{m}$ radius size particle investigated by Calspan. It is not possible to measure the critical supersaturation of soluble particles greater than $0.1\text{ }\mu\text{m}$ with the TGDCC. The reason for this is that particles which are that large start to appear as droplets in the TGDCC even at subsaturated humidities and therefore, it is not possible to detect the critical point at which the particle is nucleated. For this reason we abandon the measurement of the solubility parameter B_0 by the method proposed earlier.

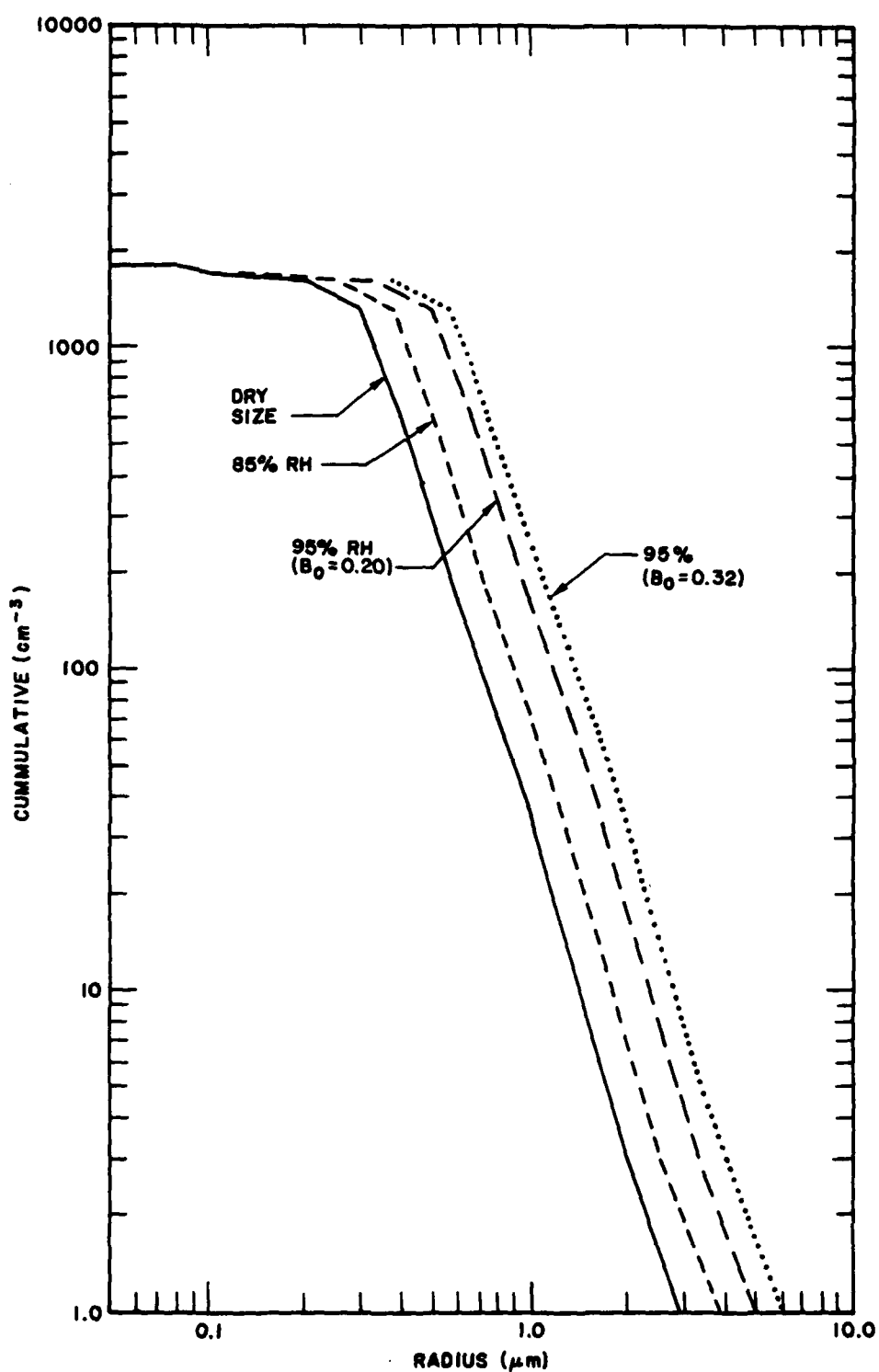


Fig. 2 — Measured cumulative dry size distribution and predicted change with increasing relative humidity

Recently NRL has constructed an isothermal haze chamber (IHC) for measuring the critical supersaturation of larger particles. In this method the size at exactly 100% RH is measured and related to the critical supersaturation. For our application particles of a predetermined dry size were transmitted to the IHC where the size range at 100% RH, r_{100} , was measured. The solubility parameter B_o is obtained from the measured values of r_d and r_{100} . The basis of this method is Eq. (2) which upon evaluation at exactly 100% RH ($S = 1$) gives the following expression for B_o :

$$B_o = \frac{A r_{100}^2}{r_d^3} \quad (7)$$

To accomplish this we set up the mobility analyzer to transmit particles in a given size range to the IHC and there measured their size at saturation r_{100} . This was done for a number of size ranges so that a correction for larger particles with multiple numbers of elementary charges could be applied. A typical result is shown in Figure 3 which shows a size histogram of the particles at 100% RH which had dry sizes in the range of 0.20 to 0.26 μm . Eq. (7) would then yield a solubility of about 0.20. It is interesting to compare this value to the value observed by Calspan for larger particles. Calspan does not

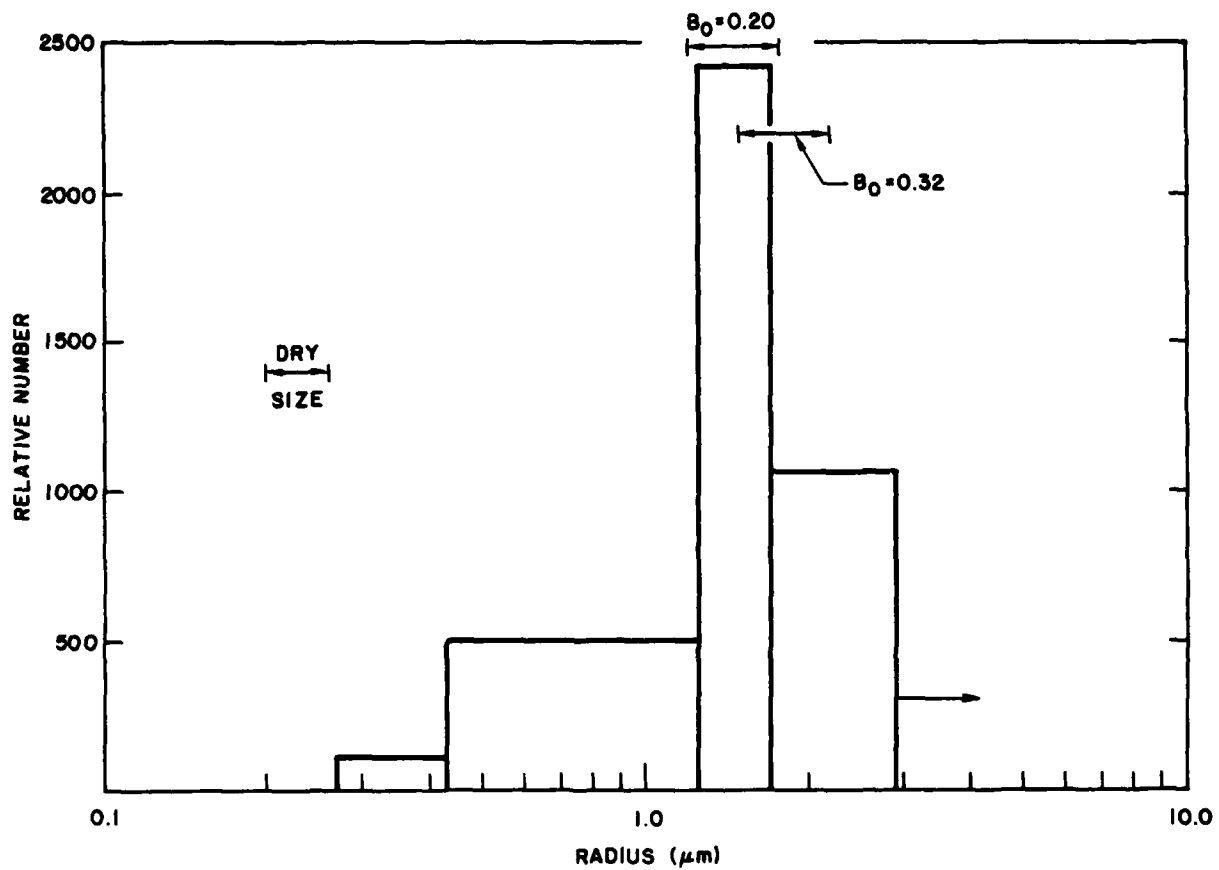


Fig. 3 — Size of particles at exactly 100% relative humidity.
Dry radius of particles was between 0.20 and 0.26 μm .

give the solubility in terms of the parameter B_0 but from their plots of growth with relative humidity a value of r_d and radius at 95% RH, r_{95} , can be obtained. These values can be plugged into Eq. (2) and the value obtained for B_0 is about 0.32. Our value of 0.20 indicates a somewhat lower value of solubility than the value of 0.32. Whether or not this difference represents a true difference in solubility between larger particles (10 μm) measured by Calspan and smaller particles measured by us, or whether this difference is within measurement error is unknown at present. Figure 3 indicates that the particle distribution at 100% RH was not as strongly peaked as would have been expected if all particles were of the same composition. It is strongly suspected that even for particles in a given size range the particles are not of uniform composition. Therefore the value of B_0 quoted must be viewed as the average solubility of the particles in that size range.

From the dry size distribution and solubility it is possible to predict the way the size distribution should change as a function of increasing humidity above the deliquescent point (80% RH). This is calculated from Eq. (6) and shown by the dashed line in Figure 2 for 85% and 95% RH for the value of B_0 (0.32) obtained from Calspan's measurements.

Recent differential size distributions taken in a Salty Dog plume during a field experiment at San Nicolas Island by Gathman (1981) for relative humidities in the range of 90 to 95% RH show a peak at about 1 μm , whereas the differential size distribution implied by the cumulative size distribution at 95% RH in Figure 2 peaks at about 0.6 μm . This would indicate that the size produced under field conditions is somewhat larger than the size distribution generated in our laboratory system and considerably larger than found in the Calspan experiment.

CONCLUSIONS AND RECOMMENDATIONS

In our measurements we found very few particles with dry radii less than 0.2 μm under a variety of conditions in a confined laboratory experiment. Calspan in a much larger chamber found many more small particles than we observed, whereas the field measurements by S. Gathman at Saint Nicholas Island would point to a distribution with sizes moderately larger than obtained in our laboratory measurements. Since the size of the particles is near that of optical wave lengths, differences in the size distribution will have a significant effect on obscuration. The differences in the size distributions may be dependent on the physical factors involved in the burning process. The explanation for the differences in the measured size distribution should be examined in future experiments. There is a real possibility that

when the physical explanation is obtained it will be of help in determining the optimum conditions (or design) for the burning of pyrotechnic material.

There seems to be some evidence that in the formation of aerosols upon recondensation of salty dog material there may be a preferential condensation of material such that small particles are less soluble than the larger particles. This phenomenon should be investigated further and if established an examination of particle composition as a function of size should be made. This could shed important information on the recondensation mechanism which forms the aerosol.

Only about a third of the material shows up as aerosol in the Calspan experiment. The missing mass is not in the very small size range as originally postulated. Therefore the mass balance should be reexamined and the disposition of the missing material ascertained.

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